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The objective of this research is to clarify the mechanisms responsible for the suppression of soot in flames by fuel additives. Measurements are limited to well-defined hydrocarbon/air prevaporized liquid- and gaseous-fueled flames. Gas-phase hydrocarbon species measurements have been made in an axisymmetric prevaporized iso-octane/air diffusion flame with and without ferrocene present as a fuel additive. The concentrations have been determined using quartz probe sampling and chromatographic analysis. Of the roughly twenty species detected, most were unaffected by the ferrocene. Exceptions were C_2H_2 and H_2 which showed a decrease and increase, respectively, with ferrocene seeding. Solid effluent has been collected and analyzed by ESCA (Electron Scattering for Chemical Analysis) for the seeded flame. For seeding levels sufficient to suppress a soot plume, the effluent was hematite.

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Investigation of Fuel Additive Effects on Sooting Flames

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Investigation of Fuel Additive Effects on Sooting Flames

PROBLEM/OVERVIEW

Fuel additives have been used effectively to suppress soot formation in both laboratory and practical flame media (Ref. 1). Since, however, the mechanism of suppression has not been established as yet, there are no criteria for additive selection and evaluation, which unfortunately has precluded their widespread use. The goal of this research is to clarify the nature of additive behavior in relation to soot control. In this research, emphasis is placed wholly on metal compounds as additives since in the past selected metals have been shown qualitatively to be very effective soot suppressants. Specifically, organo-iron compounds as well as inorganic alkali and alkaline-earth salts are the principal objects of study in this program. The metals are introduced into small laboratory-scale laminar flames. Since such flames are well defined, their study optimizes the prospect of clarifying additive behavior. Both diffusion and premixed flames are included in this research since the latter flame types may be shown to complement each other significantly. In all circumstances, measurements are carried out or planned for gaseous fuels alone. This includes the diffusion flame fueled by iso-octane and described below since the liquid fuel is heated and vaporized prior to combustion. One of the objectives of this program is to establish the one or more soot formation stages at which the additive intervenes. This is not a trivial task since its execution requires the measurement of both gaseous and particulate flame species. To this end, both in-situ laser as well as sampling probe measurements are relied on. The laser is used principally, though not exclusively, to characterize soot particulates, whereas the sampling probe and subsequent gas chromatographic analysis is used to characterize soot precursor species.

In our last report to AFOSR (Ref. 2), we described light scattering measurements which were carried out on soot and Fe_xO_y particulates formed in a prevaporized iso-octane/air diffusion flame seeded with ferrocene. The ferrocene was observed to eliminate the soot plume of a flame operating initially above its smoke point and, in general, to reduce soot near the flame's apex. Suppression was due to both soot size and number density reduction. In contrast, a slight enhancement in sooting was observed for measurements made in the vicinity of the burner lip. Accordingly, ferrocene was observed to have the property of either decreasing or increasing soot depending upon the exact measurement location. In addition to soot, evidence was found for the presence of Fe_xO_y particulates in the seeded flame. The latter were observable as light scattering signals which were spatially separated and, thus, distinct from those due to soot, and which were enhanced in intensity by adding a trace of O_2 to the fuel stream. The Fe_xO_y were observed to form temporally prior to soot and, hence, to serve possibly as nucleation sites for incipient soot formation.

During the past year progress has been made in two specific areas. First, the effect of ferrocene on gas-phase hydrocarbon species formed in the flame has been determined

from quartz probe measurements coupled with gas-chromatographic concentration analysis. Second, the solid effluent from the seeded flame has been collected above the flame and analyzed for chemical composition via ESCA (Electron Scattering for Chemical Analysis). The latter two areas of activity are discussed in more detail below.

PROGRESS

Quartz Probe Measurements

In order to determine the effect, if any, which ferrocene has on the gas-phase products of iso-octane/air combustion, the latter species concentrations have been measured using a small quartz probe for species extraction, a steel cylinder for sample collection, and a gas chromatograph for concentration analysis.

The probe used by us is shown in Fig. 1. It is uncooled, has a 0.17 mm diam. aperture, and is similar to one used earlier by Kaiser et al. (Ref. 3). The design of the probe is such as to minimize flame perturbations and to effect a rapid reduction in static pressure and thereby quench species-altering chemical reactions occurring within the probe or transfer line. Using a mechanical vacuum pump and an appropriate control (throttle) valve, the pressure at the probe tip was typically 1-3 Torr under conditions of sampling, i.e., with the probe positioned within the luminous zone of the flame. Pressures higher than the range given above showed evidence of perturbations of the true flame species spectrum, i.e., additional species not present at 1-3 Torr were evident.

The gas handling system used to collect samples extracted by the probe is shown in Fig. 2. With it, species may be collected in a steel sample bottle at room temperature, or collected at liquid nitrogen temperature in a u-tube attached to the control valve. The control valve was used to set the probe tip sampling pressure which was measured with the capacitance manometer. The steel bottle was used successfully to collect gas-phase species up to about C_{10} . The role of the u-tube was to trap condensable, higher molecular weight species such as the pcah; however, this was not successful since the probe became plugged before a condensate of sufficient quantity could be collected. Plugging was not a problem for gas-phase species collection since probe insertion times, relative to those for condensate collection, were very short. In summary, the data reported here are for non-condensable species only. The latter, after being allowed to fill the sample bottle for 1 min or so, were taken then to a separate gas chromatographic facility for analysis.

Two different flames were studied in this work. One was fueled by prevaporized (135°C) iso-octane mixed with air, while the other differed from the first in that it had a 0.3% (by weight) ferrocene additive present in the starting liquid fuel. The burner and related apparatus are shown in Fig. 3. Pure iso-octane or one of several different iso-octane/ferrocene mixtures is selected with the rotary switch. The positive displacement pump delivers about 200 microliters/min of liquid to the vaporizer. There the liquid im-

pacts a column of heated (135°C), small steel spheres (not shown in Fig. 3), vaporizes, and is purged through the burner tube with a small $\sim 60\text{cc/min}$ N_2 flow. The vertical portion of the burner tube is more complex in construction than indicated in Fig. 3. A thin cartridge heats the top portion of the burner tube directly through an intermediate slip-fit slotted plug. The cartridge heater and its leads are isolated from the hot fuel vapor and the leads are brought out through a feed-through at the bottom of the burner tube. The chimney has a hole in one of its sides through which the quartz probe is inserted. The probe itself is attached to coupled, programmable translation stages which permits precise x- and z-positioning of the probe tip relative to the burner lip.

The flame studied in this work operates above its smoke-point without ferrocene present. As such, the soot loading is heavy, which leads to rather rapid plugging of the probe's aperture; under the best conditions, sampling could be done for a period not exceeding 1-2 min. Since soot loading varies with height, the preceding difficulty translates into a finite vertical range over which measurements were possible. That is, species sampling could be done for $z \leq 15$ mm, or for vertical positions up to but not including those of peak pcah and soot concentration. An attempt was made to collect pcah (at liquid nitrogen temperature) at $z = 15$ mm with and without ferrocene, but the permissible sampling period was too short for adequate sample collection.

Despite the limitations outlined above, a reasonably large number of species was detected in the range $0 < z < 15$ mm. Figure 4 lists all of the species observed at $z = 15$ mm. The numbers in parentheses are the statistical mole % errors multiplied by 100; so that, e.g., 3.12 (18) is 3.12 ± 0.18 , etc. The total mole fraction in Fig. 4 is 25.56%; the remaining species are presumed to be N_2 and O_2 , where the latter (i.e., O_2) was not readily amenable to mole percent measurement with our gas chromatograph. In order to account more carefully for all species, at least for one sample position, the O_2 content of a sample at $z = 9$ mm was analyzed with a calibrated mass spectrometer and found to be present at $2.7 \pm 0.5\%$ concentration. When this is added to an estimated 70% N_2 concentration from gas chromatographic analysis, and then added to the concentrations of the remaining species, a 104% concentration results. This, for our purposes, is close enough to the correct value of 100% since relative (and not absolute) concentrations with and without ferrocene are of principal interest here.

With the exception of naphthalene (C_{10}H_8), as indicated by the large error, all the measured mole fractions were very repeatable. We believe the difficulty with naphthalene to have been its tendency to condense in undesired locations either during collection or during analysis. For this reason, although it is an important pcah, we make no claim to have successfully measured its concentration. Generally, Fig. 4 indicates that ferrocene is not very perturbing of the species mole fractions. The possible exceptions are C_2H_2 , H_2 and CO . Figures 5 through 9 give the representative behavior of the more important species concentrations as a function of vertical position. In contrast with the absence of

any perturbation of C_6H_6 in Fig. 5, ferrocene appears to decrease C_2H_2 systematically and to increase H_2 dramatically in Fig. 6. Although the measurement errors associated with C_2H_2 and H_2 measurement are not small, we believe that the indicated trends are probably correct. If so, a possible conclusion to be drawn from these data is that ferrocene enhances C_2H_2 oxidation. Although an increase in CO was observed only at $z = 15$ mm in Fig. 7, the increase is consistent with the foregoing hypothesis. Also in Fig. 7 the pyrolysis of the fuel behaves very similarly with and without ferrocene, which is evidence against any significant increase or decrease of flame temperature due to ferrocene introduction. The total O_2 (or $2O$), C and H_2 data in Figs. 8 and 9 gives evidence that the gross composition of the unseeded and seeded flames are very similar.

ESCA Particulate Analysis

In premixed ethylene/air flames seeded with ferrocene, Ritrievi et al. (Ref. 4) have presented evidence that the ferrocene combustion product Fe_xO_y is occluded by the soot particulates, and that under favorable conditions the additive species may diffuse to the surface of the particulate and enhance soot oxidation. More specifically, the chemical state of the additive species within the soot and its ability to diffuse to the surface of the particulate determines the extent to which both growth and oxidation are affected.

In view of the above, experiments were carried out in order to look for occlusion in our flame. Since probe plugging prevented our sampling particulates from within the luminous zone, collection was done above the flame tip and well into the post flame effluent stream. There a water-cooled aluminum disk was placed for some tens-of-minutes, and a visible condensate was allowed to form. The sample was then subjected to chemical composition analysis versus depth using ESCA (Electron Scattering for Chemical Analysis). In this technique, the material to be analyzed is illuminated with a beam of soft x-rays. These cause both photo- and Auger-electrons to be emitted from surface layer atoms. Measurement of the kinetic energies of the emitted electrons may be converted to binding energies from which a species identification may be made. The atom fraction of a given element is a function of the area under the signal curve and an appropriate sensitivity factor. Depth profiles are obtained by controlled sputtering away of surface material with energetic argon cations done in sequence with the ESCA procedure described above. The ESCA sample analysis was done for us by Dr. Bruce L. Laube of our laboratory.

As mentioned, the unseeded flame in this experiment operates above its smoke-point. For a 0.3% ferrocene seed, the flame goes over to below smoke-point operation, and a red-orange condensate covers the aluminum disk. The results of the ESCA analysis of this condensate is shown in Fig. 10. The results for the surface layer (i.e., zero Å depth) are spurious in that the carbon present results most likely from atmospheric CO_2 contamination. This occurred since no special precautions were made to shield the sur-

face once sample collection was complete. The data at 50, 100 and 200 Å are, however, correct and indicate clearly that the condensate is Fe_2O_3 . This provides no direct evidence concerning occlusion since carbon was not detected below the outermost surface layer. In view of this, samples were collected for conditions of very slight ferrocene seeding (smoke plume still visible, 0.01% ferrocene by weight in fuel). In this case, the condensate was principally carbon with, however detectable quantities of iron present. The chemical state of the additive was elemental iron (Fe), and the results of the depth profile were inverse to that expected for occlusion. In summary, we found no evidence for occlusion of Fe_xO_y by soot in our diffusion flame. This contrasts with the opposite conclusion reached by Ritrievi et al. (Ref. 4) for measurements in a premixed flame.

Summary

Gas phase species measurements in the range $\text{C}_1 - \text{C}_9$ have been made in an axisymmetric diffusion flame with and without ferrocene present. The concentrations have been determined using quartz probe sampling and chromatographic analysis. Of the roughly twenty species detected, most were unaffected by the ferrocene. Exceptions were C_2H_2 and H_2 which showed a decrease and increase, respectively, with ferrocene seeding. A possible interpretation of this observation is that the additive accelerates acetylene oxidation. It was our intention to probe heavier species, such as the pcah, as well. This, however, was not possible for the specific flame described herein. For it the soot loading is very large in the region of near peak pcah concentration. Consequently, insertion of the sampling probe into the latter region results in plugging of the probe orifice in a time less than that required for collecting a quantity of pcah sufficiently large to exceed minimum detection standards.

Solid effluent has been collected and analyzed by ESCA for the seeded flame. For seeding levels sufficient to suppress a soot plume, the effluent was Fe_2O_3 , which is consistent with our indirect observation of this particulate from light scattering data described in our previous annual report to AFOSR (Ref. 2). We were not successful in verifying the occlusion of the Fe_2O_3 by soot and, hence, are unable to support or deny catalytically enhanced oxidation of soot by Fe_2O_3 as a suppression mechanism.

NEAR TERM PLANS

During the coming year, work on the diffusion flame will be brought to a conclusion, and additional effort will be focused on metals added to premixed flames.

For the diffusion flame, we plan to try even more intensely to extract Fe_xO_y and sample species in regions of the luminous zone corresponding to peak or near peak soot concentration. This will be done by using probes having a larger aperture and/or sampling leaner flames.

For the premixed flame, the metals of choice will most likely be the alkalis and/or alkaline-earths. Since ferrocene has been studied carefully by Rittrévi et al. (Ref. 4), we feel no urgency to repeat their effort. The premixed flame work which we intend to pursue will provide an easier environment for probing species and understanding additive behavior than is the case for a diffusion flame. A premixed flame burner has been constructed and the related experiments are ready to begin.

ACKNOWLEDGEMENTS

I am grateful to Dr. Meredith B. Colket, III for guiding me through the probe measurements, and to Dr. Bruce L. Laube for doing the ESCA sample analysis.

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2. Bonczyk, P. A.: Laser-Induced Saturated Fluorescence of SrOH in Flames. *Appl. Opt.* (in review).
3. Bonczyk, P. A., and Colket, M. B., III: Suppression of Soot by Ferrocene in a Diffusion Flame (in preparation).

PERSONNEL

The research described in this report was carried out principally by Dr. Paul A. Bonczyk, Senior Research Scientist, Combustion Sciences. Dr. Meredith B. Colket, III, Senior Research Scientist, Combustion Sciences, participated in analyzing the probe measurements. Dr. Bruce L. Laube, Associate Research Engineer, Materials Analysis, carried out the ESCA measurements.

INTERACTIONS

On 15-17 June 1988, Dr. Paul A. Bonczyk participated in the 1988 AFOSR/ONR Contractors Meeting on Combustion, Monrovia, Calif.

QUARTZ SAMPLING PROBE

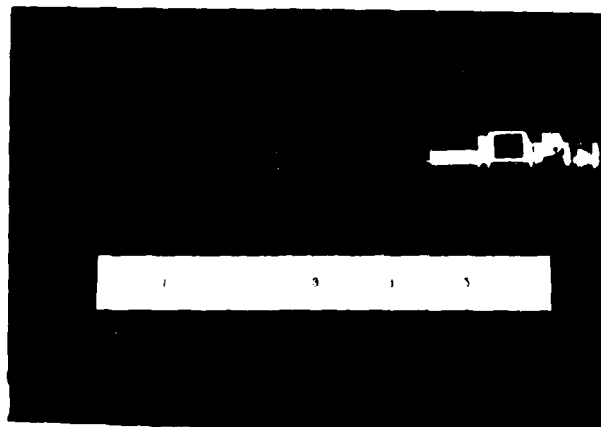
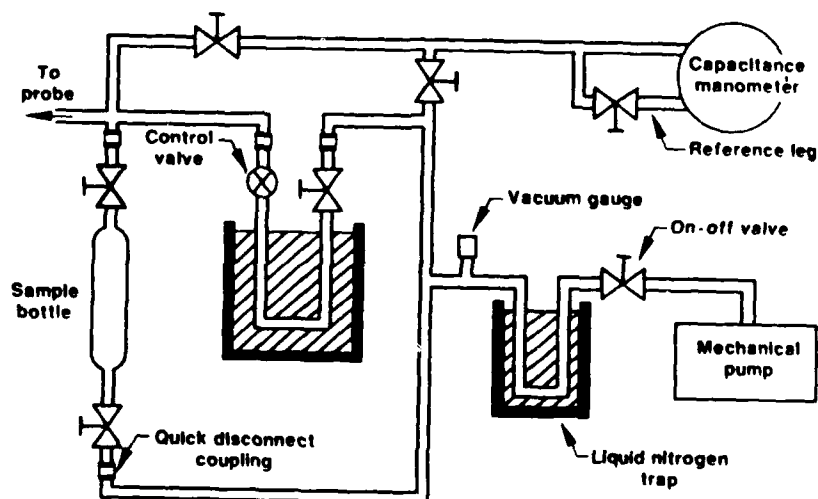


FIG. 2

SPECIES SAMPLING SCHEMATIC



PREVAPORIZED FUEL BURNER

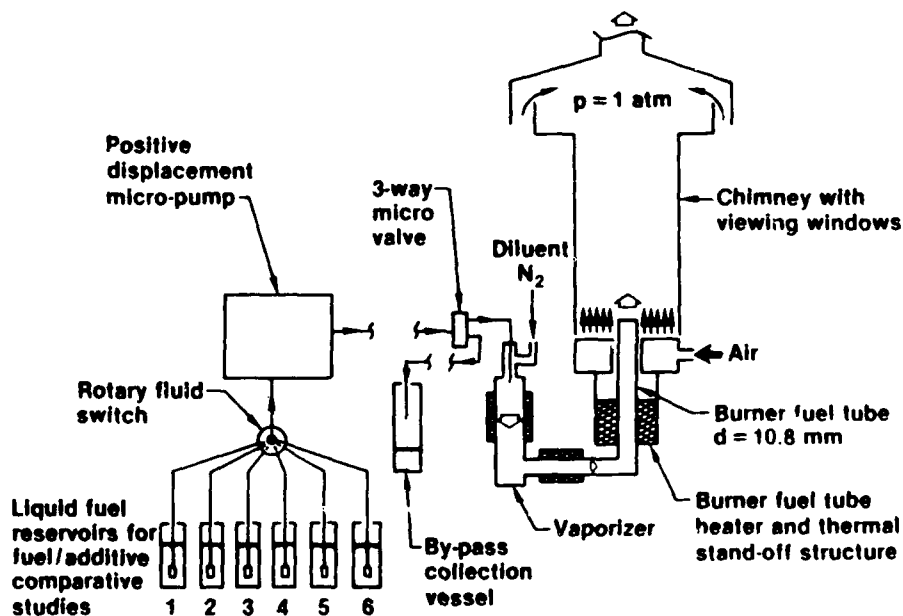


FIG. 4

GAS CHROMATOGRAPHIC SPECIES ANALYSIS RESULTS

Species mole fractions at 15 mm height with and without ferrocene.
Measurement uncertainties are given in parentheses.

Species	Mole % without ferrocene	Mole % with ferrocene
CH ₄	3.12 (18)	3.35 (23)
C ₂ H ₂	2.19 (22)	1.75 (40)
C ₂ H ₄	1.44 (8)	1.43 (8)
C ₂ H ₆	0.14 (2)	0.11 (5)
C ₃ H ₄	0.58 (8)	0.46 (12)
C ₃ H ₆	0.33 (8)	0.35 (12)
C ₃ H ₈	0.09 (3)	0.08 (2)
Isobutene	0.14 (5)	0.15 (9)
C ₄ H ₆	0.54 (2)	0.52 (7)
C ₄ H ₈	0.10 (3)	0.13 (5)
phenylacetylene	0.08 (2)	0.06 (4)
styrene	0.11 (3)	0.10 (4)
C ₆ H ₆	0.10 (5)	0.05 (3)
C ₁₀ H ₈	0.31 (28)	0.37 (41)
H ₂	3.98 (60)	7.60 (219)
CO	4.90 (21)	6.32 (33)
CO ₂	7.41 (30)	7.83 (72)

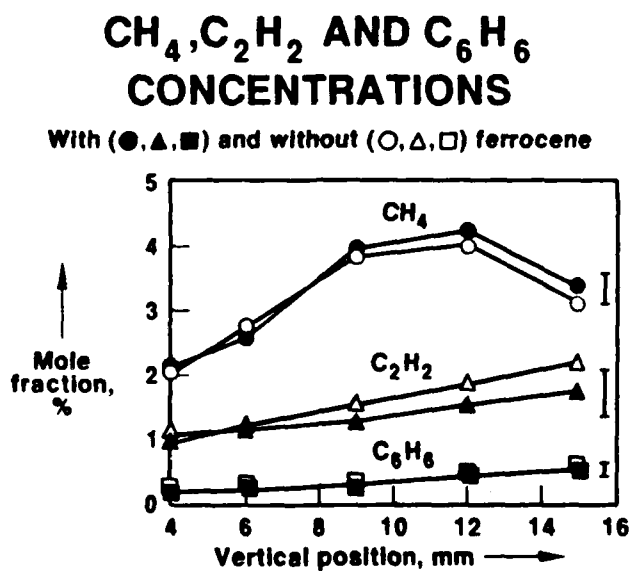
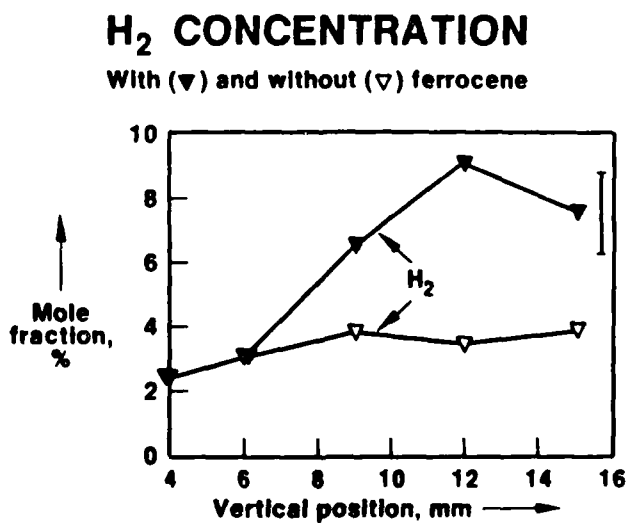


FIG. 6



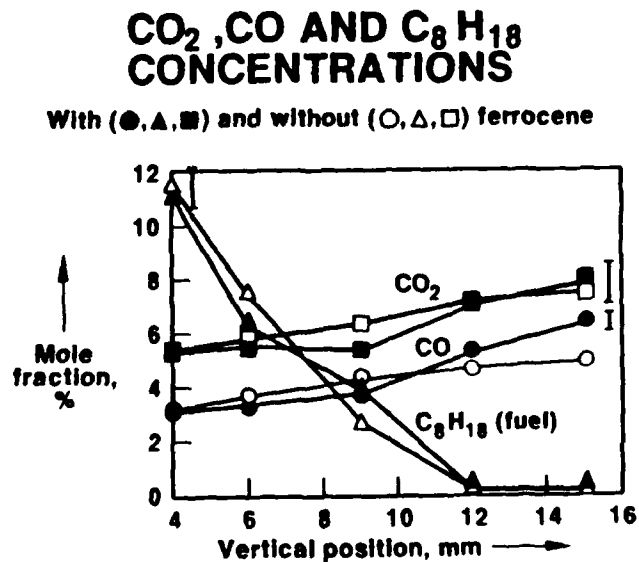
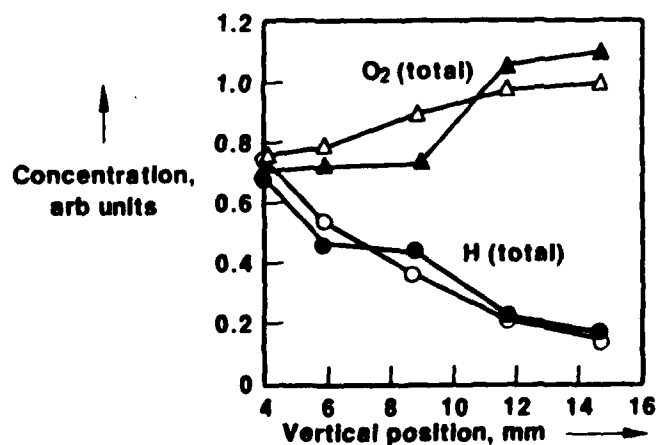


FIG. 8

TOTAL O₂ AND H CONCENTRATIONS

With (▲, ●) and without (△, ○) ferrocene



TOTAL O₂ AND C CONCENTRATIONS

With (Δ , ∇) and without (\triangle , \triangledown) ferrocene

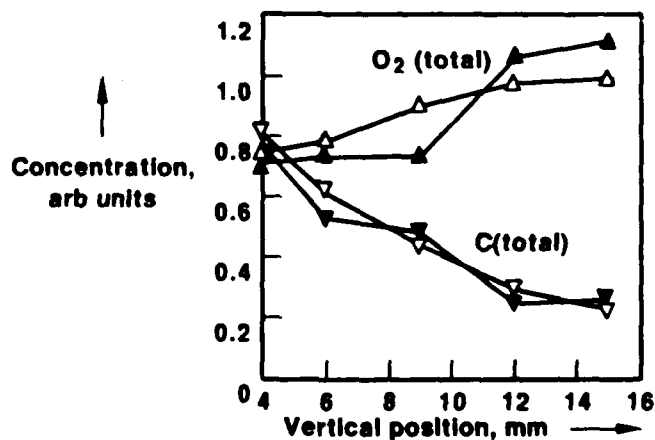


FIG. 10

ESCA ANALYSIS OF FLAME DEPOSITS

Composition of effluent in atomic percent units.
Ferrocene in fuel at 0.3% (wgt). Below smoke-point flame.

Depth, Å	Fe	O	C
0	32.0	53.1	14.8
50	40.4	58.2	1.1
100	43.6	56.4	-
200	43.3	56.7	-